Scanning Photoemission Microscopy Characterization of the Pyrite FeS$_2$ (001) Natural Surface

E.M. Kneedler[1], K. Pecher[2] and B.P. Tonner[1]

[1]Dept. Of Physics, University of Central Florida, Orlando, FL 32816, USA

[2]Caltech, California 94720, USA

INTRODUCTION

The study of pyrite has been mainly driven by its prominence in aqueous environmental systems and by its possible usefulness as a photovoltaic material. Pyrite is the most abundant sulfide mineral, and often coexists in ores of other desired minerals. The behavior of pyrite in mineral deposits in various aqueous environments is of great concern. The release of H_3O^+ and concomitant drop in pH resulting from pyrite surface oxidation can lead to the release of more toxic metals such as Cd, Pb, Zn and Cu, commonly referred to as acid mine drainage. Pyrite has been identified as a medium for the uptake and possible reduction of toxic uranyl U(VI) compounds.[1] In that study, it was proposed that partial reduction to uranium U(IV) may be correlated with the oxidation state of the pyrite surface, based on an apparent correlation of U sorption sites with pyrite oxidation zones. However, the separation of pyrite surface oxide from uranyl compound oxygen signals is not straightforward with conventional techniques, and the issue is further complicated by a gradual photo-reduction of U(VI) to U(IV) caused by incident x-rays.

We are focused on two issues: pyrite oxidation processes in general, and the sorption of uranyl compounds and their subsequent reduction. In the case of oxidation, it is difficult to distinguish pyrite oxide signals from those arising from oxide impurities. In a parallel experiment, we are characterizing the clean pyrite surface through XPS and X-ray photoelectron diffraction (XPD) measurements of the S$_{2p}$ core level.[2] It is important rule out possible contributions from oxide-related features to establish the intrinsic pyrite structure.

In sorption studies, where the kinetics can vary greatly depending on the substrate composition, it is important to establish whether the deposits are associated with the nominal mineral surface or occur only in the vicinity of impurities. In both cases, Scanning Photoemission Microscopy (SPEM) is a valuable technique for separating signals from trace impurities from the overall XPS signal. The SPEM chamber employs a zone-plate scheme which focuses the synchrotron beam to ~150 nm. The sample is stationary during imaging and the zone plate is rastered in the illumination field to carry the focused spot across the sample surface. An order sorting aperture (OSA) is positioned within 0.5 mm of the sample surface, and the zone plate assembly is cut back on one side to allow a line of sight for the PHI spectrometer. The zone plate/OSA used for this study was optimized for hν~705 eV, the energy used in our experiment. A light sputter/anneal method was chosen to prepare pyrite samples for its capability to produce a clean, flat, and stoichiometric surface.
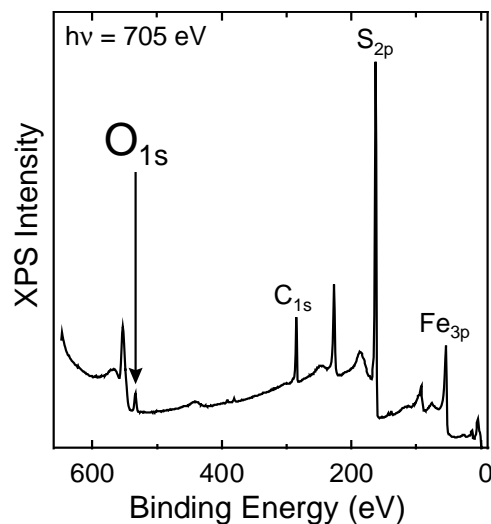

Figure 1. Conventional XPS of pyrite FeS$_2$ (001) surface. The surface was prepared by light sputter/annealing. Small amounts of oxygen are always detected. A carbon overlayer develops over time in ambient UHV.
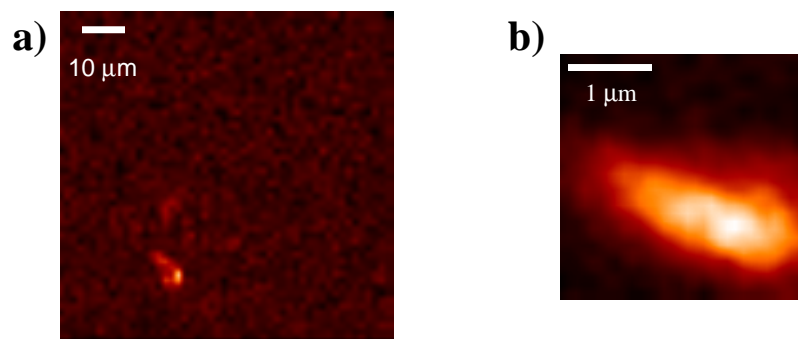
Figure 2. Scanning Photoemission Microscopy (SPEM) images of the FeS_2 (001) surface. Contrast represents the relative concentration of oxygen. a) A typical 80 x 80 μm region, showing one major feature. b) Detailed image of an oxygen impurity elsewhere on the sample. Photon energy was 705 eV.

RESULTS

A conventional XPS survey of a natural pyrite surface cleaned by sputter/annealing is shown in Figure 1. Carbon can always be removed by this cleaning method, but gradually accumulates on the surface over a period of days in ambient UHV; this spectrum was acquired one week after cleaning. In addition to the characteristic FeS_2 signature, a relatively small amount of oxygen is present, and could not be removed by repeated sputter/anneal cycles. To establish whether the S and Fe levels in XPS and XPD measurements accurately represent clean (unoxidized) pyrite, we measured the distribution of the oxygen using the SPEM chamber on BL7.0.1. The SPEM image shown in Figure 2 represents the contrast between the signal at the O 1s core level (527 eV BE) and the adjacent background (520eV BE). A single prominent feature is visible in Fig. 2a, representing a high concentration of oxygen. The detailed image in Fig. 2b shows another feature elsewhere on the sample. We have found that the vast majority of the surface contains negligible amounts of oxygen except in sparse concentrated regions.

To identify the character of the nominal clean pyrite surface as well as features such as in Fig. 2, we obtained spectra, shown in Figure 3, with the beam focused on and away from these features. A typical spectrum representing a featureless region is shown in Fig. 3a. Oxygen is absent from this area of the sample, and the only impurity seen in the spectrum is carbon. Much of the carbon can be attributed to signal from the zone plate, and the rest is a result of the gradual carbon deposition from one week exposure to ambient UHV (the two carbon contributions can be separated by biasing the sample by -5V to separate the peaks, as seen in the spectra). This result gives credence to our
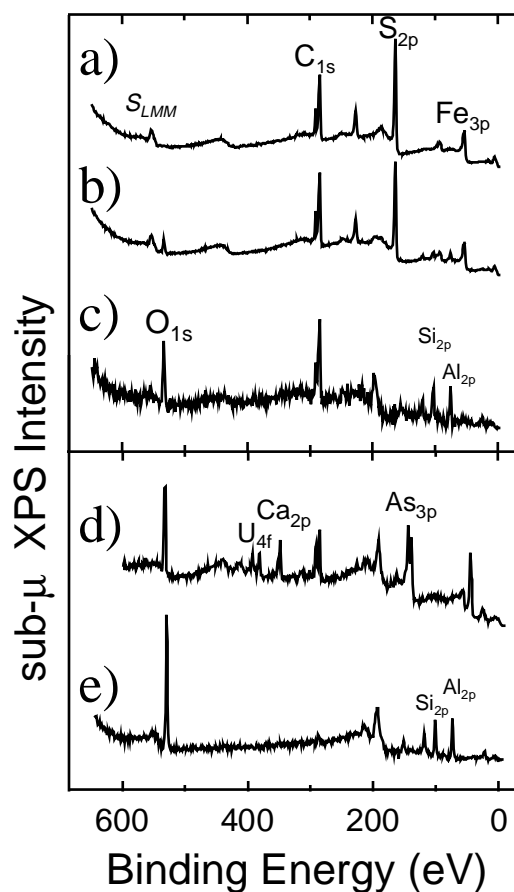

Figure 3. Spectra of FeS_2(001) surface using a zone-plate system with an incident spot size of 0.15 μm. Spectra represent a) a pure region, b) an impurity, c) impurity with FeS_2 component subtracted, d) & e) other impurity difference spectra. Photon energy was 705 eV.

assumption that oxidized pyrite is not represented in the S_{2p} core level structure in the XPS and XPD measurements of clean pyrite.[2] In Fig. 3b, with the beam focused on the feature seen in Fig. 2b, the spectrum shows significant Si, Al, and O signals, and a reduced signal from Fe and S, suggesting an aluminosilicate mineral inclusion. An accurate signature of the inclusion, shown in Fig. 3c, was obtained by subtracting the FeS_2 component of Fig. 3a from Fig. 3b. Difference spectra from other impurities are shown in Figs. 3d and 3e. We found several inclusions with similar composition to Fig. 3d, containing U, As, and Ca. In other spectra (not shown) we have identified also Pb, and $CaCO_3$ inclusions. The trace presence of U, Pb and other heavy metals as well as As in natural pyrite is well known, but we were surprised by their relative abundance. The consistent coexistence of U and As on the sub-micron scale suggests a mineralogical association. For instance, the deposition of U may be promoted by the presence of As through a reductive process. It is clear from these measurements that a sub-micron characterization of the surface is necessary before conducting uranyl sorption studies to identify already existing U and possible reactive sites.

It is also important to consider the presence of inclusions in measurements of sorbed species such as oxygen. The reactivity of defect sites could be enormously different than for the pure FeS_2 surface, and it would be difficult to isolate their contribution to "oxidation". Indeed, several studies have reported very little chemical change in Fe and S core levels, while observing the adsorption of H_2O, OH, and related species.[3] Such inclusions are likely a general feature of natural pyrite surfaces, however they may easily go undetected with less surface-sensitive x-ray lamp XPS.

CONCLUSION

We have used SPEM to better characterize a typical natural FeS_2 (001) surface. The small oxygen signal seen in conventional XPS is seen to be concentrated in trace mineral inclusions. The S_{2p} core level structure we have observed in parallel XPS and XPD experiments is thus intrinsic to unoxidized pyrite. We have identified several trace impurities in the inclusions: U, As, Ca, C, Si, Al, Pb, and of course O. U is always accompanied by As in our measurements, suggesting that they are associated. It will be essential to characterize a given sample region in this way before and after sorption studies to establish the nature of the sorption process.

REFERENCES

[1] P. Wersin, M.F. Hochella, P. Persson, G. Redden, J.O. Leckie, and D.W. Harris, "Interaction between aqueous uranium (VI) and sulfide minerals: spectroscopic evidence for sorption and reduction", Geochim. Cosmochim. Acta **58**, 2329 (1994).

[2] E.M. Kneedler, K. Pecher, and B.P. Tonner, *to be published*.

[3] S.W. Knipe, J.R. Mycroft, A.R. Pratt, H.W. Nesbitt, and G.M. Bancroft, "X-ray photoelectron spectroscopic study of water adsorption on iron sulphide minerals", Geochim. Cosmochim. Acta **59**, 1079 (1995).

Principal investigator: Brian Tonner, Department Of Physics, University of Central Florida, Orlando, FL
Email: tonner@csd.uwm.edu. Telephone: 407-823-2325